DOI: 10.1002/ ((please add manuscript number))

**Article type:** Full paper

Highly efficient flexible hybrid nanocrystal-CIGS solar cells

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Keywords: Scattering, Luminescent Down Shifting, Nanocrystal Quantum Dots, Hybrid Photonics, Flexible CIGS

We demonstrate a novel scheme for hybridizing inkjet-printed thin film Cu(In,Ga)Se2 (CIGS) solar cells with self-assembled clusters of nanocrystal quantum dots (NQDs) that provides a 10.9% relative enhancement of the photon conversion efficiency (PCE). A non-uniform layer of NQD aggregates is deposited between the transparent conductive oxide and a CdS/CIGS p-n junction using low cost pulsed-spray deposition. Hybridization significantly improves the external quantum efficiency of the hybrid devices in the absorption range of the NQDs and in the red to near-IR parts of the spectrum. The low wavelength response enhancement is found to be induced by luminescent down-shifting (LDS) from the NQD layer, while the increase at longer wavelengths is attributed to internal scattering from NQD aggregates. LDS is demonstrated using time-resolved spectroscopy, and the morphology of the NQD layer is investigated in fluorescence microscopy and cross-sectional transmission electron microscopy. The influence of the NQD dose on the PCE of the hybrid devices is investigated and an optimum value is obtained. The low costs and limited material consumptions associated with pulsed-spray deposition make these flexible hybrid devices promising candidates to help push thin-film photovoltaic technology towards grid parity.

**1. Introduction**

With lab-scale efficiencies exceeding 20%[1], thin film Cu(In,Ga)Se2 (CIGS) solar cells have established themselves as frontrunners of thin-film photovoltaic (PV) technology. The intrinsic qualities of polycrystalline CIGS, such as its high absorptivity, band-gap tunability and easy grain boundary passivation, have attracted a lot of attention since the early days of PV technology.[2] Their compatibility with high throughput roll-to-roll processing could allow a drastic reduction of the device cost and payback time compared to traditional vacuum co-evaporation or sputtering techniques.[3] Typical CIGS solar cells are deposited on a rigid glass, flexible stainless steel or plastic substrate coated with a layer of molybdenum that acts as a back contact and reflector. A thick (2 µm) p-type CIGS absorber and thin (~50 nm) n-type CdS buffer layer are subsequently deposited to form a CdS/CIGS heterojunction. The devices are terminated with a thin intrinsic ZnO widow layer (~50 nm) and an Al:ZnO (AZO) transparent conductive oxide (TCO) layer (see **Figure 1**). An important drawback of this device stack architecture is the poor response of the solar cells in the UV to green part of the spectrum, due to the strong optical absorption of the CdS buffer, ZnO window and AZO TCO layers.[4,5] The strong doping asymmetry between the CIGS and CdS layers confines the depletion region into the CIGS. This inhibits the extraction efficiency of the carriers generated in the CdS layer and results in large quantum efficiency losses at lower wavelengths. Luminescent down-shifting (LDS) provides a simple scheme to mitigate this issue. In this approach, a luminescent material deposited on or integrated into the device absorbs high energy photons and reemits below the band-gap of the buffer, window or TCO layers, optically pumping the absorber and generating efficiently extractable carriers.[6,7] Both organic dyes[8-11] and quantum dots[12-15] have been extensively investigated as LDS materials for numerous PV technologies suffering from similar limitations,[8-15] such as III-V and cadmium telluride solar cells.[8-13,16] The high absorptivity in the UV band, narrow emission spectral range, good absorption and emission tunability and high quantum yields of NQDs make them especially well-suited for such applications.[17,18] Previous attempts to implement LDS in CIGS solar cells focused on depositing luminescent material onto the AZO layer and resulted in relative low efficiency enhancements between 3 and 5%.[19-21]

In this work, we report on the successful incorporation of self-assembled clusters of CdSe/ZnS core/shell NQDs into flexible CIGS solar cells. The NQDs are embedded between the CdS buffer and the ZnO window layer using pulsed-spray deposition (see **Figure 1**). We leverage the poor uniformity of spray deposited NQD layers to engineer an integrated luminescent and light scattering layer of self-assembled NQD aggregates. The nanocrystals are tuned to emit below the band-gap of CdS, with an emission wavelength of 560 nm, and LDS is found to provide an important enhancement of the quantum efficiency within the absorption range of the NQDs. The NQD clusters also provide a large increase of the PCE in the red to near-IR spectral range. The NQD aggregates scatter the incident light and displace the absorption closer to the CIGS/CdS interface, where the depletion field is strongest, which consequently increases the average extraction efficiency of the photogenerated carriers. The morphology of the NQD aggregates is investigated using luminescence microscopy and cross-sectional transmission electron microscopy (TEM), while LDS is characterized using time-resolved spectroscopy. An optimum NQD dose is obtained and hybridization is found to result in a 10.9% relative enhancement of the PCE.

**2. Results and discussion**

The PV devices studied consist of a Al:ZnO(250 nm)/ZnO (50 nm)/NQDs/CdS(50 nm)/CIGS(2 μm)/Mo(800 nm) layer stack deposited on a stainless steel substrate, as depicted in **Figure 1**a and **1**b. The air pressure pulsed-spray deposition system used to deposit the NQD layer is illustrated in **Figure 1**c. The NQDs used in this study are colloidal CdSe/ZnS core-shell nanocrystals dispersed in toluene with a photoluminescence quantum yield (QYNQD) of ~40%. Reference (without NQDs) and hybrid devices were fabricated side-by-side on the same 4 cm2 sample to eliminate sample to sample disparities. **Figure 2** shows the photoluminescence (PL) and absorption spectra of spray coated NQDs on a glass substrate, along with the absorption spectrum of bulk CdS on glass. The emission wavelength of the NQDs (560 nm) is chosen so as to minimize absorption from CdS. At higher wavelengths, CdS becomes transparent and the buffer layer allows transmission of the incident light into the underlying CIGS absorber.

The in-plane morphology of the NQD aggregates was studied using dark field fluorescence microscopy. A 2 μm thick CIGS layer capped with a 50 nm CdS thin-film was investigated before and after deposition of 9 pulses of NQDs. The weak dark-green non-uniform PL signal in the bare sample (**Figure 3**a) is attributed to the bulk CdS emission. The hybridized sample exhibits bright emission from a non-uniform mesh of NQD aggregates as shown in **Figure 3**b. Micrometer-wide features spanning 10 to 100 µm in length can be observed. Such a morphology is characteristic of the self-assembly of spray deposited NQDs during solvent evaporation.[22] The lateral size of the NQD aggregates was further investigated using cross-sectional TEM in two CdS/CIGS p-n junctions coated with 9 and 17 pulses of NQDs (**Figure 3c** and **Figure 3**d). In these images, the NQD aggregates are visible as a pale grey region embedded between the darker CdS layer and the black carbon support. 3-5 nm diameter nanoparticles could clearly be resolved using higher magnifications and were confirmed to be CdSe/ZnS NQDs using energy-dispersive X-ray spectroscopy (EDS) (see Supporting Information). Hybridization with 9 pulses of NQDs is found to form thin (~10 nm) aggregates with a lateral spatial extension of ~500 nm. Aggregation is found to be more pronounced in the case of the 17-pulse deposition, with thicknesses in excess of 300 nm and lateral sizes ranging between 1 and 2 µm. The 17-pulse deposition is thus expected to induce a high series resistance at the ZnO/CdS interface, detrimental to the device performance.

The external quantum efficiency (EQE) and current-voltage (J-V) characteristics of the hybrid and reference devices were investigated for various NQD doses, by varying the number of NQD spray pulses between 1 and 17. The relative variations in short-circuit current density (JSC) (**Figure 4**a), photon conversion efficiency (PCE) (**Figure 4**b), open-circuit voltage (VOC) and fill factor (FF) (**Figure 4**c) between each hybrid device and its corresponding reference device are presented as a function of the number of NQD pulses (see Supplementary Information for additional data). The variations in device series resistance RS are derived from the slope of the J-V curves near open-circuit condition (**Figure 4**a). The 9-pulse deposition is found to provide the maximum JSC enhancement. The initial increase of the JSC enhancement at lower NQD doses is attributed to an increased contribution of LDS and of internal scattering on NQD aggregates. The decrease of the JSC above 9 pulses is due to the gradual emergence of an additional series resistance at the CdS/ZnO interface, as shown in **Figure 4**a. This interpretation is further corroborated by the cross-sectional TEM study, which showed that high NQD doses promote the assembly of thick clusters larger than the CIGS grains (~1 µm) (**Figure 3**c and 3d**)**, which strongly impede the extraction of the minority carriers. The PCE variations (**Figure 4**b) are principally driven by the JSC, and the PCE dependence on the NQD dose follows closely the behavior of the JSC. Hybridization is found to be slightly detrimental to the VOC for lower NQD doses (**Figure 4**c), the NQDs acting as recombination centers at the CdS/ZnO interface. The VOC increase above 9 pulses is attributed to scattering on NQD aggregates, which lowers the average penetration depth of the longer wavelength photons and limits bulk recombination in the CIGS layer. Contrary to the VOC, the FF displays a net enhancement at lower doses and a reduction above 9 pulses (**Figure 4**c). The initial enhancement is attributed to LDS of the solar spectrum, which displaces carriers away from the CdS/ZnO interface and limits the space-charge screening of the depletion field. The reduction of the FF for higher NQD doses is a consequence of the increase in series resistance. The low FF of the 1-pulse sample was found to be related to an increased shunt resistance, possibly due to a poor homogeneity of the CdS layer. The J-V characteristics of the optimized 9-pulse hybrid solar cell and of its corresponding reference device are presented in **Figure 4**d. The 9-pulse hybridization is found to provide the best overall performances, with a relative increase in of 12.2% (31.9 mA/cm2 to 35.5 mA/cm2) yielding a large 10.9% relative enhancement of the PCE (8.42% to 9.34%).

The EQE enhancement dependence on the NQD dose was investigated by measuring the hybrid and reference EQEs for various numbers of NQD spray pulses (see Supporting Information). A 9-pulse NQD deposition is again found to be optimal, in good agreement with the JSC dependence on the NQD dose. The absorptivity of the 9-pulse hybrid and reference samples was measured in an integrating sphere and was found to be weakly impacted by hybridization (< 1%), thus discarding any potential anti-reflection coating effect. The EQE of the 9-pulse hybrid solar cell and its corresponding reference device are presented in **Figure 5**, along with the relative EQE enhancement. Hybridization with 9 pulses of NQDs is found to induce two regions of pronounced EQE enhancement at lower and higher wavelengths. The rapid enhancement in the lower part of the spectrum corresponds to the absorption range of the NQDs and is attributed to LDS. The NQDs are directly photo-excited and the resulting photoluminescence is absorbed in the CIGS layer to generate extractable carriers, thus enhancing the overall quantum efficiency of the device. Above 560 nm, the NQDs are non-absorbing and the EQE enhancement is attributed to scattering of the incident photons on NQD aggregates. The embedded NQD aggregates offer a good refractive index contrast to the surrounding ZnO/CdS interface (nNQDs = 2.5, nZnO = 1.94 and nCdS = 2.34 at 1000 nm) and act as efficient scattering centers. The contributions of LDS and of scattering on NQD aggregates to the photocurrent of the hybrid device can be estimated using the following equation:

(1)

where and are the EQEs of the hybrid and reference devices, respectively, is the photon flux of the AM1.5G solar spectrum (ASTMG173), is the current density relative enhancement due to hybridization, and where the integration is done between 300 nm and 560 nm for the LDS contribution and between 560 nm and 1300 nm for the scattering component. Using this analysis, LDS and scattering on NQD aggregates are estimated to contribute 1.9% and 8.1% of the JSC enhancement due to hybridization. The significant contribution of LDS to the total photocurrent of the hybrid device reinforces the interest of using luminescent material as a scattering layer.

LDS in the NQD layer was demonstrated using a 470 nm pulsed laser diode and time-resolved spectroscopy, by monitoring the PL decay of CIGS in a hybrid NQD/CdS/CIGS structure and in a reference CdS/CIGS sample (red and black curves respectively in **Figure 6**). The bi-exponential dynamics of CIGS is found to be noticeably slower in the hybrid sample compare to the reference case, which indicates the presence of an additional slower pumping channel. The PL decay dynamics of the NQDs in the hybrid sample (blue curve in **Figure 6**) is observed to be slower than the fast component of the CIGS decay dynamics. The PL decay of the NQDs was fitted with a stretched exponential function to account for the distribution of lifetimes in the NQDs, yielding an average lifetime of 4.79 ns. The CIGS dynamics was found to display a strong non-exponential behavior and was modelled using the universal equation for free minority carrier recombination[23]

(1)

which can be analytically solved to provide the excess minority carrier population in CIGS :

(2)

where and are the linear and quadratic recombination decay rates of CIGS, corresponding to the low and high injection regime respectively. During the early times of the PL decay, the excess minority carrier density, estimated to be ~1019 cm-3, is much larger than the typical net acceptor density of CIGS films (~1016-1017 cm-3).[23,24] The decay dynamics is then driven by the quadratic term and the PL signal decays rapidly. When the excess minority carrier density decreases, linear recombination become dominant and the PL signal of CIGS starts decaying exponentially. A best fit to the measured decay curve of the reference CIGS sample yielded linear and quadratic decay times of 24.6 ns and 1.2 ns respectively, in good agreement with previous reports.[25] In the case of the hybrid NQD/CIGS solar cell, the PL dynamics of CIGS was modeled using two coupled rate equations:

(3)(4)

where is the average decay rate of the NQDs, measured experimentally, is the absorption of the NQDs at 470 nm, is the quantum yield of the NQDsand (t)is a Kronecker delta function. A least squares optimization technique was used to fit the CIGS decay dynamics in the hybrid sample. A value of = 0.12 was obtained, in good agreement with absorption measurements of NQD films on glass. The LDS contribution to the CIGS PL, given by , is found to be ~5.5%. Taking into account the variation in EQE between 470 nm and 560 nm, this LDS contribution corresponds to an EQE relative enhancement of 8.4%, in good qualitative agreement with the measured 11% EQE relative enhancement at 470 nm. This analysis provides further evidence of the presence of a significant LDS pumping channel for the CIGS absorber in the hybrid NQD/CIGS devices.

**3. Conclusion**

In this study, the successful integration of self-assembled aggregates of luminescent nanocrystal quantum dots (NQDs) into flexible CIGS solar cells is demonstrated, yielding an ~11% relative enhancement in photon conversion efficiency. Luminescent down-shifting in the NQDs and internal scattering of the incident light on self-assembled nanoparticle aggregates induce a large increase of the external quantum efficiency, in excess of 50% at 320nm. The low-cost pulsed-spray processing technique used to deposit the NQDs makes this approach easily scalable and cost-effective, while the high deposition rates make it compatible with high-throughput roll-to-roll manufacturing. In this work, we utilize the self-aggregation of NQD clusters, typical in spray deposited NQD layers, to engineer an efficient light management scheme that significantly improves the efficiency of hybrid CIGS devices. The incorporation of luminescent colloidal NQDs into hybrid photonics devices is believed to be a promising approach to help tackle the energy challenges of tomorrow.

**4. Experimental Section**

*Fabrication of the CIGS solar cells*

The copper oxide (CuO), indium oxide (In2O3) and gallium oxide (Ga2O3) have been mixed with a Ga/(In+Ga) ratio of 0.3 and a Cu/(In+Ga) ratio of 0.8~1 in deionized water. The wet stirred milling process was then used with a small amount of surfactant to avoid nanoparticle aggregation, transforming particles with an initial size of a few micrometers into particles with size of only 50-80nm in a stable non-flocculated state. The solid content of the stable ink was measured to be about 0.2 g/ml. A doctor blade was used to coat the precursor film on a Mo/Cr/stainless steel (SS) substrate. The precursor was then reduced in an H2 atmosphere at 450°C for 30 minutes, before being annealed in an H2Se atmosphere and in an H2S atmosphere at 400°C for 30 minutes and 500°C for 30 minutes, respectively. The CIGSeS absorption layer was rinsed in a KCN (5 wt%) solution to remove the excess CuSe. The CdS buffer was deposited using Chemical Bath Deposition (CBD) in a cadmium sulfate, thiourea and ammonium hydroxide solution. Before deposition, all substrates were rinsed with DI-water to prevent air voids. All substrates were blow-dried using nitrogen after deposition. Finally, the CdS/CIGSeS layer was coated with a transparent conductive oxide (TCO) using sputtering deposition, and a silver contact grid was deposited using a printing process.[26] The resulting device structure is a Al:ZnO (250nm) / ZnO (50nm) / CdS (50nm) / CIGS (2μm) / Mo(800 nm) layer stack on a stainless steel substrate.

*Deposition of nanocrystal quantm dots*

A solution of colloidal ZnS/CdSe core-shell NQDs procured from Sigma Aldrich (Lumidot 560 in toluene, 0.08 mg/ml) was dispensed onto the surface of the CdS layer using air pressure pulsed-spray deposition. The NQDs displayed a 1s absorption and emission peak of 525 nm and 526 nm, respectively. In traditional spraying techniques, the viscosity of the spraying mixtures can considerably affect the uniformity of the finished film. The interaction between the particles in the pre-mixed solution A solution of colloidal ZnS/CdSe core-shell NQDs in toluene with a concentration of 0.08 mg/ml was dispensed onto the surface of the CdS layer using air pressure pulsed-spray deposition. The NQDs displayed a 1s absorption and emission peak of 525 nm and 526 nm, respectively. In traditional spraying techniques, the viscosity of the spraying mixtures can considerably affect the uniformity of the finished film. The interaction between the particles in the pre-mixed solution.

*Optical measurements*

A 470 nm pulsed diode laser was used for the spectrally-resolved and time-resolved photoluminescence (PL) measurements. The repetition rate of the laser was 4 MHz for the spectrally-resolved measurements and 0.5 MHz for the time-resolved measurements. The excitation power was kept constant at 0.5 mW and the excitation beam was focused at normal incidence with a 20 cm lens. The PL signal of the CIGS and of the NQDs was collected at an oblique angle with a 10 cm lens, transferred to a monochromator and detected by a an avalanche photodiode (PicoQuant PDM series) connected to a TCSPC acquisition card (PicoQuant TimeHarp 200). All PL measurements were taken at room temperature. A UV-VIS-NIR spectrophotometer (Hitachi U4100) equipped with standard mirror optics and an integrating sphere was used to measure the absorption of the solar cells. An Olympus BX51M brightfield/darkfield reflected light microscope equiped with Olympus UIS2 fluorescence mirror units and an Olympus DP26 digital camera was used to obtain bright and dark field images of the samples. The samples were excited with a filtered mercury lamp (BP330-385) and the photoluminescence signal was collected by an objective (Olympus MPLFFLN20x) and filtered with a long-pass filter (BA420) and a dichroic mirror (DM400). All fluorescence images were taken with an integration time of 80 ms and a magnification of 12.6x.

*Electrical characterisation*

Current-voltage measurements were performed following the procedure described in the international standard CEI IEC 60904-1. All solar cells were characterized under a simulated Air Mass 1.5 Global (AM1.5G) illumination with a power of 1000W/m2. The temperature was actively controlled during the measurements and was kept at 25±1 °C. The power conversion efficiency (PCE) measurement system consisted of a 1000 W Class A solar simulator (Newport 91192A) equipped with a Xenon lamp (Newport 6271A), an AM1.5G filter (Newport 81088A) and a current-voltage source (Keithley 2400). The spectrum of the solar simulator was measured with a calibrated spectroradiometer (Soma S-2440) between 300 to 1100 nm. The external quantum efficiency (EQE) of the devices was measured using a 300 W Xenon (Newport 66984) light source and a monochromator (Newport 74112). The system was calibrated before each measurement with a calibrated silicon photodetector. The EQE measurements were carried out using a lock-in ampliﬁer (Standard Research System, SR830), an optical chopper unit (SR540) operated at 260 Hz and a 1 Ω resistor in shunt connection.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge support from the European Nanophotonics for Energy Efficiency Network of Excellence and the Ministry of Economic Affairs, Taiwan. The authors would also like to acknowledge Prof. Yu-Lun Chueh of the Department of Materials Science and Engineering, National Tsing-Hua University for his support. Prof. P. G. Savvidis gratefully acknowledges financial support from the Leverhulme Trust.

Received: ((will be filled in by the editorial staff))  
Revised: ((will be filled in by the editorial staff))  
Published online: ((will be filled in by the editorial staff))

[1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, *Prog. Photovolt: Res. Appl.* **2014**, *22*, 701.

[2] National Renewable Energy Laboratory (NREL), Best Research-Cell Efficiencies, http://www.nrel.gov/ncpv/images/efficiency\_chart.jpg.

[3] A. Chirilă, S. Buecheler, F. Pianezzi, P. Bloesch, C. Gretener, A. R. Uhl, C. Fella, L. Kranz, J. Perrenoud, S. Seyrling, R. Verma, S. Nishiwaki, Y. E. Romanyuk, G. Bilger, A. N. Tiwari, *Nat. Mater.* **2011**, *10*, 857.

[4] F. Engelhardt, L. Bornemann, M. Köntges, Th. Meyer, J. Parisi, E. Pschorr-Schoberer, B. Hahn, W. Gebhardt, W. Riedl, U. Raw *Prog. Photovol. Res. Appl.* **1999**, *7*, 423.

[5] K. Orgassa, U. Rau, Q. Nguyen, H. W. Schock, J. H. Werner, *Prog. Photovol. Res. Appl.* **2002**, *10*, 457.

[6] H. C. Chen, C. C. Lin, H. V. Han, K. J. Chen, Y. L. Tsai, Y. A. Chang, M. H. Shih, H. C. Kuo, P. Yu, *Sol. Energy Mater. & Sol. Cells* **2012**, *104*, 92.

[7] H. C. Chen, C. C. Lin, H. W. Han, Y. L. Tsai, C. H. Chang, H. W. Wang, M. A. Tsai, H. C. Kuo, P. Yu, *Opt. Express* **2011**, *19*, A1141.

[8] E. Klampaftis, D. Ross, K. R. McIntosh, B. S. Richards, *Sol. Energy Mater. Sol.* *Cells* **2009**, *93*, 1182.

[9] B. S. Richards, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2329.

[10] X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.* **2013**, *42*, 173.

[11] C. P. Thomas, A. B. Wedding, S. O. Martin, *Sol. Energy Mater. Sol. Cells* **2012**, *98*, 455.

[12] H.-J. Muffler, M. Bär, I. Lauermann, K. Rahne, M. Schröder, M. C. Lux-Steiner, C.-H. Fischer, T. P. Niesen, F. Karg, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 3143.

[13] H. C. Chen, C. C. Lin, H. V. Han, K. J. Chen, Y. L. Tsai, Y. A. Chang, M. H. Shih, H. C. Kuo, P. Yu, *Sol. Energy Mater. Sol. Cell*s **2012**, *104*, 92.

[14] Z. Cheng, F. Su, L. Pan, M. Cao, Z. Sun, *J. Alloys Compd*. **2010**, *494*, L7.

[15] S. D. Hodgson, W. S. M. Brooks, A. J. Clayton, G. Kartopu, V. Barrioz, S. J. C. Irvine, Nano Energy **2013**, *2*, 21.

[16] L. Danos, T.Parel, T.Markvart, V.Barrioz, W.S.M.Brooks, S.J.C.Irvine, *Sol. Energy Mater. Sol. Cells* **2012**, *98*, 486

[17] Q. Sun, Y. A. Wang, L. S. Li, D. Y. Wang, T. Zhu, J. Xu, C. H. Yang, Y. F. Li, *Nat. Photonics* **2007**, *1*, 717.

[18] K. J. Chen, H. C. Chen, K. A. Tsai, C. C. Lin, H. H. Tsai, S. H. Chien, B. S. Cheng, Y. J. Hsu, M. H. Shih, C. H. Tsai, H. H. Shih, H. C. Kuo, *Adv. Funct. Mater.* **2012**, *22*, 5138.

[19] H. J. Muffler, M. Bär, I. Lauermann, K. Rahne, M. Schröder, M. C. Lux-Steiner, C. H. Fischer, T. P. Niesen, F. Karg, *Sol. Energy Mater. & Sol. Cells* **2006**, *90*, 3143.

[20] G. C. Glaeser, U. Rau, *Thin Solid Film* **2007**, *515*, 5964.

[21] E. Klampaftis, D. Ross, S. Seyrling, A. N. Tiwari, B. S. Richards, *Sol. Energy Mater. & Sol. Cells* **2012**, *101*, 62.

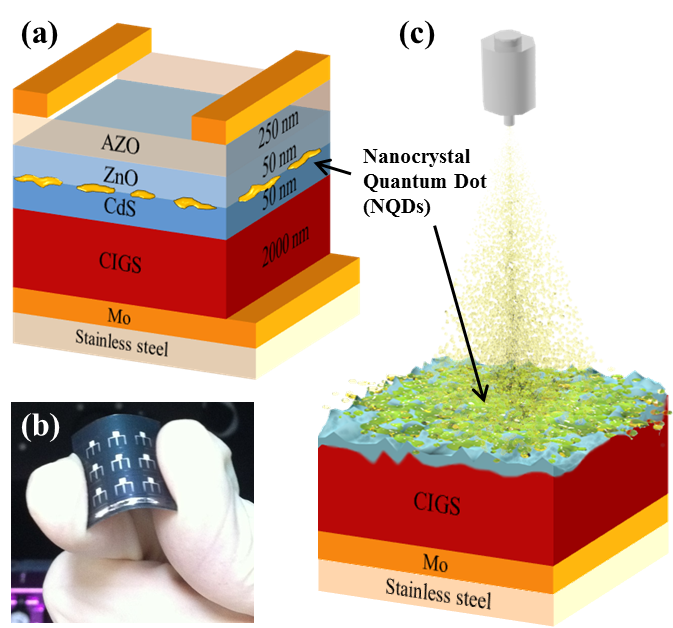
[22] W. Han, Z. Lin, *Angew. Chem. Int. Ed.* **2012**, *51*, 1534.

[23] B. Ohnesorge, R. Weigand, G. Bacher, A. Forchel, W. Riedl, F. H. Karg, *Appl. Phys. Lett.* **1998**, *73*, 1224.

[24] M. Gloeckler, A. L. Fahrenbruch, J. R. Sites, *Proceedings of 3rd World Conference on Photovoltaic Energy Conversion* **2003**, *1*, 491.

[25] S. Shirakata, T. Nakada, *Thin Solid Film* **2007**, *515*, 6151.

[26] W. T. Hsu, C. C. Cjiang, T. Y. Chuang, L. T. Cheng, L. P. Wang, S. W. Chan, K. Y. Lai, W. C. Chen, H. T. Cheng, C. C. Li, J. C. Chang, Y. Y. Tsai, S. Y. Tsai, *Proceedings of 37th IEEE Photovoltaic Specialists Conference (PVSC)* **2011**, 2034.



**Figure 1.** (a) Schematic illustration of a flexible inkjet-printed NQD/CIGS hybrid solar cell. (b) Photograph of a hybrid device. (c) Schematic illustration of the pulsed-spray NQD deposition system.

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Figure 2.** Absorption spectrum of a CdS thin-film on glass (blue, dashed line) and absorption/photoluminescence spectra of the NQDs (orange, dashed and solid line) on glass.

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Figure 3.** Fluorescence microscopy images of a CdS/CIGS junction before (a) and after (b) NQD hybridization. Cross-sectional TEM images of CdS/CIGS junctions coated with 9 (c) and 17 (d) NQD spray pulses.

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Figure 4.** (a) Relative variations of the JSC (black) and of the Rs (red). (b) Relative variations of the PCE. (c) Relative variations of the VOC (black) and of the FF (red). (d) J-V characteristics of the optimized 9-pulse hybrid solar cell (red) and its corresponding reference device (black).

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Figure 5.** (a) EQE of the hybrid (red) and reference (black) devices for a 9-pulse NQD deposition. (b) Relative EQE enhancement due to hybridization.

  
**Figure 6.** Photoluminescence decay dynamics of CIGS in a reference CdS/CIGS sample (black) and of CIGS and the NQDs in a hybrid NQD/CdS/CIGS sample (red and blue, respectively). The green dashed curve is a best fit to the CIGS dynamics in the hybrid sample using a rates equations model.

**Low-cost pulse-spray deposition is used to incorporate self-assembled clusters of luminescent nanocrystal quantum dots (NQDs) into a flexible thin-film CIGS solar cell.** Luminescent down-shifting and internal scattering on NQD clusters are found to provide a large broadband improvement of the quantum efficiency yielding a 10.9% relative increase of the efficiency.

**Scattering, Luminescent Down Shifting, Nanocrystal Quantum Dots, Hybrid Photonics, Flexible CIGS**

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Highly efficient flexible hybrid nanocrystal-CIGS solar cells

